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Synthesis, crystal and electronic structure of $Li_8Zn_2Ge_3$, a compound displaying an open layered anionic network

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Abstract

A better interpretation of the electrochemical behavior of the compound Li_2ZnGe as a negative electrode material for lithium batteries has forged the need to revisit the pseudo binary Li–(Zn,Ge) system. The crystal structure of Li_2ZnGe was found ordered in the cubic $F\bar{4}3m$ space group ($a = 6.123(1)$ Å), it was refined both from ambient temperature powder pattern, using the Rietveld method and from single crystal intensities recorded at $-100\,^{\circ}C$. The new compound $Li_8Zn_2Ge_3$ has been discovered in the Li-rich domain and its structure determined from single crystal in the trigonal R3c space group ($a = 7.555(1)$, $c = 24.449(3)$ Å). The originality of the compound $Li_8Zn_2Ge_3$ arises from its hexagonal ZnGe anionic layer in which the 1/3 vacancy on the Zn site is compensated by two lithium atoms. Theoretical analysis on the basis of EHT and DFT periodic calculations has provided informations on the electronic properties and bonding within the planar hexagon-based ZnGe network in $Li_8Zn_2Ge_3$.

Keywords: Intermetallic phases; Lithium Zintl phases; Germanium–zinc anionic layers; Crystal structures; Density functional calculations

1. Introduction

The need for more performing and secure anodic materials in lithium-ion batteries than those based on carbon has boosted research in various domains. Lithium/post-transition element (Al, Si, Sn, Sb…) binary systems have been widely investigated. Generally, drastic volumic and structural changes occur in these systems, associated with lithium electrochemical exchanges, that generate significant damage leading to a rapid fading on cycling and loss in the cell capacity.

It has been shown that these problems could be partially palliated by the use of ternary lithium alloys [1,2]. Our investigations of lithium/transition or late-transition/post-transition element systems were motivated by the good electrochemical properties found in some lithium-transition metal-pnictides, lithium–aluminum-silicides and germanides.

The phase diagram of the pseudo-binary Li–(Zn,Ge) published more than twenty years ago [3] reports the existence of two intermetallic compounds: $Li_{1.25}ZnGe$ that decomposes peritectically at 620 °C and Li_2ZnGe that melts congruently at 785 °C. On the other hand, authors report the existence in the Li-rich domain of a phase δ (Li_3ZnGe) decomposing at about 497 °C. Li_2ZnGe was found to crystallize in two polymorphs: cubic above 502 °C and trigonal below [3,4]. $Li_{1.25}ZnGe$, whose crystal structure was described as disordered in the trigonal space group P3 [5], was later reformulated LiZnGe with its structure refined in the hexagonal space group $P\bar{6}m2$ [6]. Recently we have tested Li–Zn–Ge alloys as potential negative electrode for lithium batteries [7]. The behavior of Li_2ZnGe has been checked against a pure lithium anode in a reversible electrochemical device. Starting from cubic Li_2ZnGe, the removal/insertion of Li was found to proceed via complex equilibria accompanied by some Ge, Zn release.

The work presented in this paper is aimed at affording additional compositional and structural information on this ternary system that will assist in the exploitation and rationalization of the electrochemical results and the design of new synthetic experiments.

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2. Experimental

LiZnGe alloys were prepared by fusion of elements inside weld-sealed tantalum tubes protected by an evacuated silica jacket. Prior to their use, the tantalum containers were cleaned with a HNO_3/HF mixture, rinsed with distilled water and finally degassed at 800 °C under high vacuum. Germanium powder (Strem chemicals, 99.999% pure) and Zn shots (Merck, analysis grade 99.9% pure) were used without further purification. Lithium (ingot, Cogema, 99.5% pure) was scraped to remove surface impurities. To avoid contamination, reagents were weighed inside a glove box filled with purified argon. Products of the reactions were handled inside the glove box and parts of them were ground into calibrated powders (20–30 μm) for powder diffraction purposes. X-ray powder patterns were recorded on a Philips analytical X'pert diffractometer equipped with a copper tube and a hybrid monochromator (parabolic multilayer mirror and two-crystal monochromator, Cu-K_α radiation). Single crystals were selected under a microscope inside the glove box, inserted into Lindemann glass capillaries and then mounted on the Xcalibur CCD (Oxford Diffraction) four-circle diffractometer for intensity measurements. The single crystal structures were solved and refined with programs SHELXS 97 and SHELXL 97 [8] and the Rietveld analysis was carried out using the program LHPM–Rietica [9]. The single crystals used for structural determinations were further analyzed by ICP emission spectrophotometry.

3. Computational details

The preliminary EHT calculations have been carried out using the program CAESAR [10]. Density functional electronic calculations were performed using the CASTEP package [11] based on the total energy plane-wave pseudopotential technique. The ion–electron interaction is modeled by an ultrasoft nonlocal pseudopotential [12] and, to reduce the number of plane waves, generated pseudopotentials were used for all atoms. The electron exchange and correlation effects were taken into account using the GGA/PBE gradient corrected approximation [13]. The energy cutoff of the plane-wave basis set was 350 eV. A Monkhorst–Pack uniform grid [14] of automatically generated k-points was used for numerical integration in the Brillouin zone. The mesh of k-points was taken as $7 \times 7 \times 7$ for the primitive cubic cell of Li_2ZnGe (4 atoms), and $4 \times 4 \times 4$ for the rhombohedral cell of $Li_8Zn_2Ge_3$ ($a = 9.244$ Å, $\alpha = 48.24°$, 26 atoms). The geometry optimizations were performed within symmetry constrained unit cells using the BFGS algorithm and ultrafine level of accuracy (energy convergence tolerance threshold of 5×10^{-6} eV/atom). SCF tolerance threshold was taken as 5×10^{-7} eV/atom (computational ultrafine level of accuracy). To obtain representations of the crystal orbitals and electron density deformation maps, calculations were also carried at Γ point using the DMOL3 quantum mechanical code [15] (GGA/PW91 approximation, DND numerical basis sets, DFT semicore pseudopotentials).

4. Results and discussion

4.1. Structure of the cubic Li_2ZnGe compound

This compound was synthesized by melting at 900 °C the elements taken in stoichiometric proportions. The crucible was hand shaken several times for good homogenization and then slowly cooled from melt to room temperature for crystallization. The X-ray powder pattern recorded at ambient temperature (Fig. 1) is characteristic of a homogeneous product and indexation of all the diffraction lines in the cubic system with $a = 6.123(1)$ Å confirms the uniqueness and purity of Li_2ZnGe (congruent melting point 780.1 °C, DSC measurement).

The transformation into the trigonal β-Li_2ZnGe has not been detected in our experiments, may be is it a metastable polymorph? The structure of Li_2ZnGe was described, twenty years ago, in the space group $Fm\bar{3}m$ ($a = 6.142$ Å) and refined from powder data to $R = 11\%$ with 10 reflections [16,17].

Rietveld refinement of the Li_2ZnGe powder data was successfully achieved in space group $F\bar{4}3m$ to $Rp = 4.5\%$ and $R_{Bragg} = 2.7\%$, with Ge at 4*b* ($U_{iso} = 0.0111(6)$ Å^2), Zn at 4*d* ($U_{iso} = 0.0163(8)$ Å^2), Li at 4*a* and 4*c* ($U_{iso} = 0.032(2)$ Å^2). Furthermore, single crystals were isolated from this preparation, the best diffracting one was selected for intensities measurements at −100 °C ($a = 6.114(1)$ Å) and subsequently analyzed (chemical analysis: Li/Zn/Ge atomic ratio = 1/0.496(2)/0.515(8)). The structure was refined in the non-centrosymmetric space group $F\bar{4}3m$ (Table 1) to $R1 = 1.7\%$ using 60 unique reflections with 6 parameters varied, the Flack parameter converged to 0.2(2), maximal (minimal) electron residual was 0.56 (−0.49) e Å^3. Refinements of both powder and single crystal data in the centrosymmetric space group $Fm\bar{3}m$ gave no satisfactory results.

4.2. Structure of the Li-rich compound $Li_8Zn_2Ge_3$

Syntheses were carried out to isolate the Li-rich phase described by Schuster as the hexagonal δ-phase Li_3ZnGe with an undetermined structure and cell parameters $a = 4.365$, $c = 8.167$ Å [3]. Instead of the phase Li_3ZnGe, single crystals of the new phase $Li_8Zn_2Ge_3$ were obtained (chemical analysis: Li/Zn/Ge atomic ratio = 1/0.253(1)/0.381(7)). The compound crystallizes in trigonal R3c space group, $a = 7.555(1)$, $c = 24.449(3)$ Å. Crystallographic and experimental details for Li_2ZnGe and $Li_8Zn_2Ge_3$ are given in Table 2 and refinement results in Table 3.

Table 1
Atomic positions and displacement parameters for atoms in cubic Li_2ZnGe ($F\bar{4}3m$)

Li_2ZnGe	Position	x	y	z	U_{iso}
Li	*4a*	0	0	0	0.02(1)
Ge	*4b*	1/2	1/2	1/2	0.0115(5)
Li	*4c*	1/4	1/4	1/4	0.04(2)
Zn	*4d*	3/4	3/4	3/4	0.0167(9)